

US-PAT-NO: 4140668

DOCUMENT-IDENTIFIER: US 4140668 A

****See image for Certificate of Correction****

TITLE: Water soluble or water dispersible hot-melt adhesive compositions based on polyvinyl alcohol with residual acetate groups and process for producing the same

----- KWIC -----

Brief Summary Text - BSTX (6):

As water soluble polymers which melt by heating, vinyl acetate-vinyl pyrrolidone copolymers and water soluble nylons are known. However, they cannot be used for bookbinding or sealing corrugated paper and cartons because they have so high a viscosity that commonly used applicators cannot be used to apply the same. Further, they have insufficient **water dispersibility or low adhesive** properties. Further, remoistenable hot-melt adhesive compositions containing partially hydrolyzed polyvinyl acetates having a degree of hydrolysis of about 50 to about 85 mol% as a main ingredient, which can be used for envelopes, postage stamps, gum tapes or wall paper, etc., have been described in U.S. Pat. No. 3,597,264. In this patent, polyvinyl alcohol having an acetate group content of about 15 to about 50 mol% (the adhesive ingredient) is produced by acid hydrolysis of an aqueous dispersion of polyvinyl acetate (hereinafter referred to as PVAc). In general, acid hydrolysis has the following defects, as described in "Polyvinyl Alcohol", pages 91 - 96, edited by C. A. Finch, (published by a Wiley-Interscience Publications (1973)): A large amount of acid catalyst and a long period of time are required to obtain a desired degree of hydrolysis because the rate of the hydrolysis reaction is very low as compared with that of alkaline hydrolysis. Further, it causes a deterioration of the quality of the polyvinyl alcohol (hereinafter referred to as PVA) because a large amount of salts are formed by neutralization with alkalis after the reaction because of the use of a large amount of acid catalyst, which salts are retained in PVA. Further, it is necessary to remove a large amount of water by evaporation in order to obtain PVA because the hydrolyzed product formed by the hydrolysis in an aqueous medium dissolves in water. As described above, acid hydrolysis is economically disadvantageous as compared with alkaline hydrolysis. Therefore, acid hydrolysis has not be utilized hitherto for the industrial production of PVA.

Brief Summary Text - BSTX (11):

An object of this invention is to eliminate the above described drawbacks of conventional hot-melt **adhesive compositions and to provide water** soluble or water dispersible hot-melt adhesive compositions which can be used for bookbinding, sealing of corrugated paper or cartons, etc., and a process for producing the same.

Brief Summary Text - BSTX (19):

The present inventors performed extensive research in order to improve various defects of prior art compositions containing a water soluble hot-melt polymer particularly PVA, and found that PVAc containing lower amounts of terminal aldehyde groups and having good heat stability avoids such defects. Further, they found that the degree of hydrolysis can easily be controlled by dissolving the PVAc mentioned above in absolute methanol at high concentration (about 60 to about 80 weight%) and hydrolyzing the same, because the hydrolysis can be stopped at any desired degree of hydrolysis (about 30 to about 60 mol%), that the amount of sodium acetate produced by alkaline hydrolysis included in the resultant PVA is decreased and the heat fusibility and heat stability are increased because of being able to decrease the amount of alkali catalyst used, that when the amount of residual volatile substances is decreased by melt-drying the caky PVA after hydrolysis foaming of the PVA at melting does not occur, that the heat stability of the PVA in the melted state is remarkably improved by adding a phosphoric acid compound thereto, and that the melting point and melt viscosity of the PVA can be controlled by changing the amount of plasticizer added thereto in relation to the average degree of polymerization of the PVA, and that the water-solubility or **water-dispersibility of the adhesive** formed therefrom can be controlled by changing the amount of the residual acetate groups in the PVA, and thus reached the present invention.

Brief Summary Text - BSTX (35):

The PVA obtained by the hydrolysis described above, the PVA having a residual acetate group content of about 30 to about 60 mol% and a degree of hydrolysis of about 70 to about 40 mol%, preferably a residual acetate group content of from about 40 to about 50 mol% and a degree of hydrolysis of from about 60 to about 50 mol%, is used as the base polymer for forming the adhesive compositions of the present invention. When PVA having below about a 30 mol% residual acetate group content is used, the resultant adhesive compositions have a high melt viscosity which deteriorates the processability thereof. On the other hand, when PVA having above about a 60 mol% residual acetate group

content is used, the water solubility or **water dispersibility of the resultant adhesive** compositions is lost and the compatibility thereof with plasticizers and the adhesive strength at high temperatures deteriorates. The residual acetate group content in the PVA is calculated from the amount of alkali necessary to produce fully hydrolyzed PVA by rehydrolysis of the partially hydrolyzed PVA. Here, the degree of polymerization of the partially hydrolyzed PVA is the same as that of the PVAc before hydrolysis. This was confirmed from the following experiment. PVAc which was produced by acetylation [in a mixture of pyridine and acetic acid anhydride (2:1) volume] of PVA having a 39.8 mol% residual acetate group content obtained by alkaline hydrolysis of PVAc having a degree of polymerization of 140 according to Example 2 had a degree of polymerization of 141.

Brief Summary Text - BSTX (39):

As the amount of the plasticizer added increases, the melting point and the melt viscosity decrease, and therefore the flexibility and the **water solubility of the adhesive** compositions improve, while the adhesive strength deteriorates and the adhesive compositions become too tacky. Accordingly, the amount of the plasticizer added should be above about $(0.08p - 10)\%$ by weight (above 0%) and below about $(0.08p + 25)\%$ by weight, based on PVA in relation to the degree of polymerization of the PVA. Adhesive compositions composed of such ingredients have a melting point of about 150 to about 180.degree. C., a melt viscosity of about 1,000 to about 8,000 cps (at 180.degree. C.) and show a good adhesive property and flexibility not only at room temperature but also at lower and higher temperatures.

Brief Summary Text - BSTX (51):

The water soluble or **water dispersible adhesive** compositions of the present invention can be used not only for bookbinding and sealing corrugated paper or cartons but also as remoistenable adhesives for postage stamps or envelopes, pasting filaments, as a heat sealing agent for water soluble PVA films and for heat-sensitive adhesives. Further, the adhesive compositions of the present invention can easily be applied using applicators as have been used for applying conventional prior art hot-melt adhesives.

Claims Text - CLTX (18):

(D) **mixing the resultant polyvinyl alcohol with the plasticizer in the above described amount and the ethylene-vinyl acetate** copolymer in the above described amount upon melting.

Claims Text - CLTX (25):

19. A process for producing adhesive compositions as set forth in claim 12 wherein the polyvinyl alcohol mixed with the plasticizer and the ethylene-vinyl acetate copolymer by melting is that produced by alkaline hydrolysis of polyvinyl acetate and drying the resultant product by melting by means of a vent type extruder.

Claims Text - CLTX (26):

20. A process for producing adhesive compositions as set forth in claim 12 wherein the step of mixing the polyvinyl alcohol with the plasticizer and the ethylene-vinyl acetate copolymer by melting is carried out by mixing the polyvinyl alcohol still containing the methanol with the plasticizer and the ethylene-vinyl acetate copolymer by melting and removing the solvent at a temperature above the melting point of the polyvinyl alcohol.

Claims Text - CLTX (32):

(D) mixing the resultant polyvinyl alcohol with the plasticizer in the above described amount, the ethylene-vinyl acetate copolymer in the above described amount and the acid compound in the amount of the above-described amount by melting.